DIAGNOSTIC CHARACTERIZATION OF BATTERY ELECTRODES

presented by

Frank McLarnon

Lawrence Berkeley National Laboratory

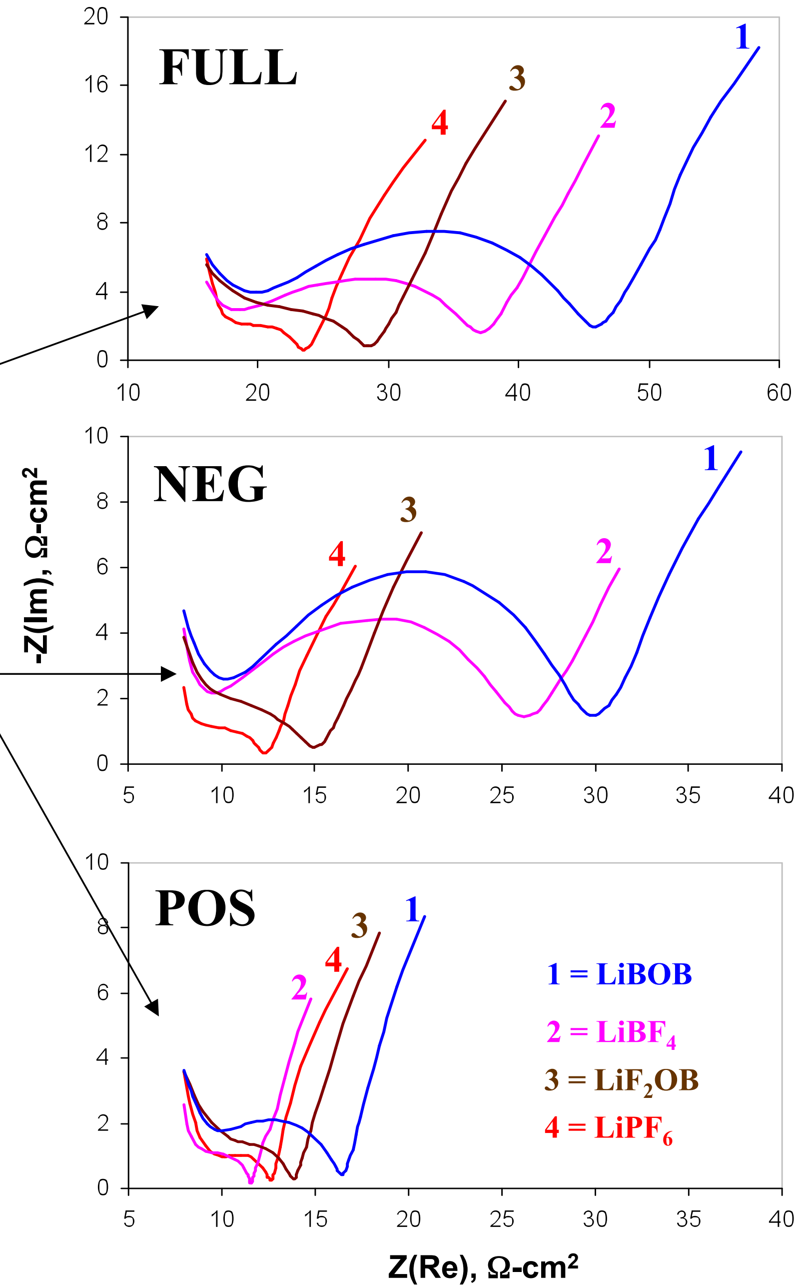
Berkeley, California 94720

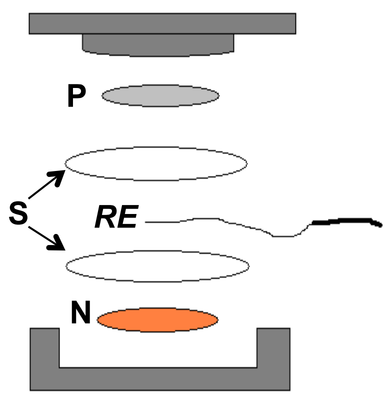
US – China Electric Vehicle and Battery Technology Workshop

August 31, 2010

Li-Sn Reference Electrode Cell Measurements

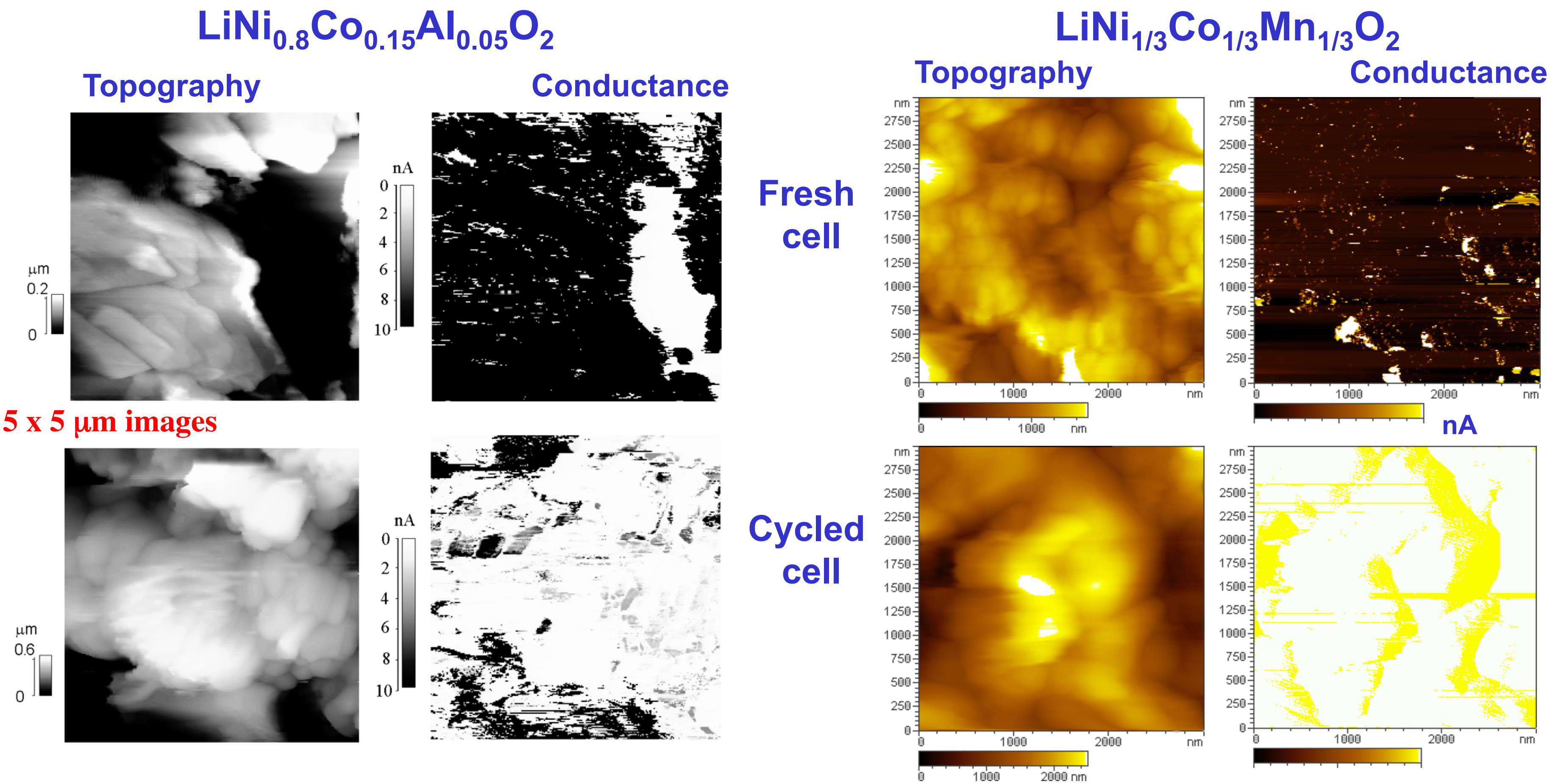
- Measurements in cells with Li-Sn reference electrodes help quantify contributions of positive and negative electrodes to cell impedance and impedance rise during cycling and aging
- Full cell data show that electrolyte salt has a significant effect on cell impedance: $LiBOB > LiBF_4 > LiF_2OB > LiPF_6$
- The negative electrode is more affected by electrolyte salt than the positive electrode
- Other data indicate that the electrolyte salt has a strong influence of SEI properties





D. Abraham, ANL

Surface Electronic Conductance Sensing AFM

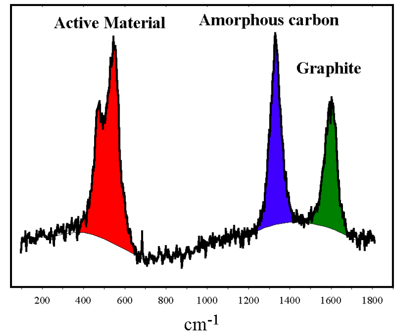


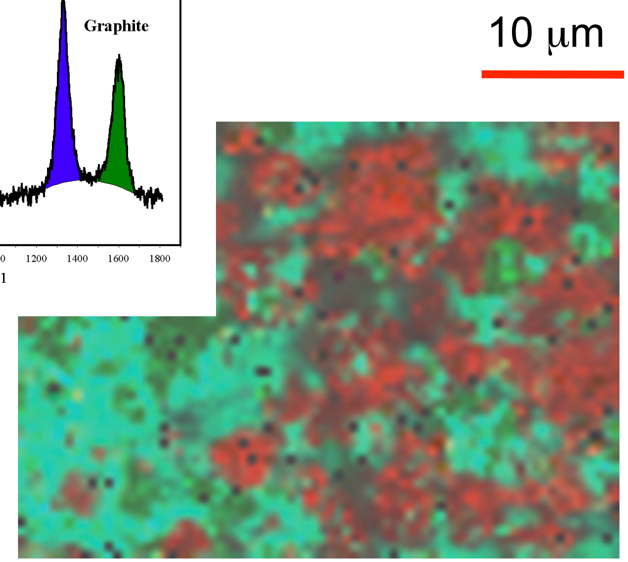
- Scanning probe microscope with an electronically conducting tip detects local electrode morphology and surface electronic conductance
- Identified changes in electrode surface morphology, surface chemistry, and SEI thickness that accompanied cell cycling

R. Kostecki, LBNL

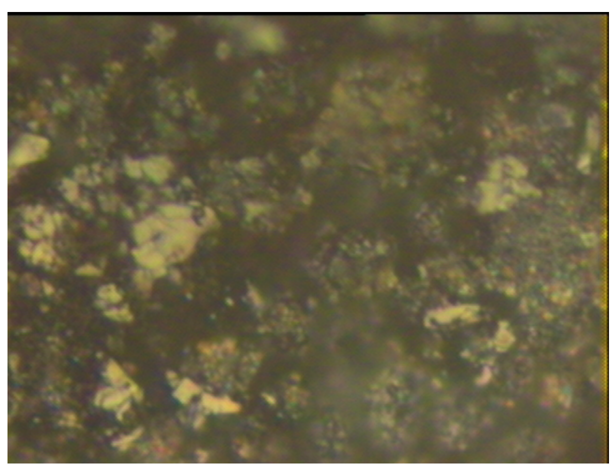
Raman Microscopy of Composite Electrodes

- Raman microscopy detects frequency shift of light scattered from an electrode
  - Probes local structure and composition
- Raman images show graphite, carbon black, and metal oxide distribution
- Revealed significant surface composition changes during cycling
- Identified carbon redistribution as a contributor to Li-ion cell power fade

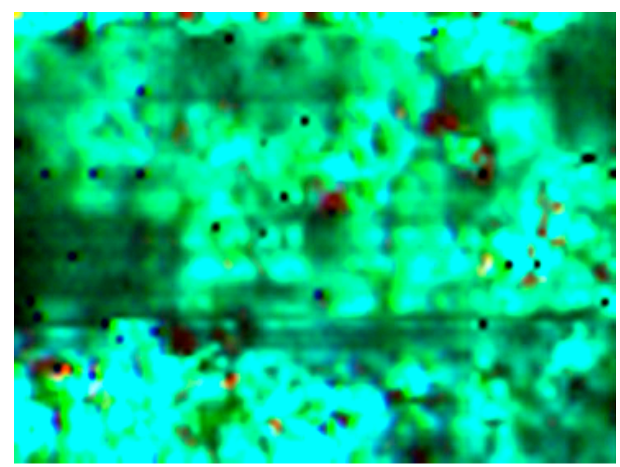




Cathode from cycled cell



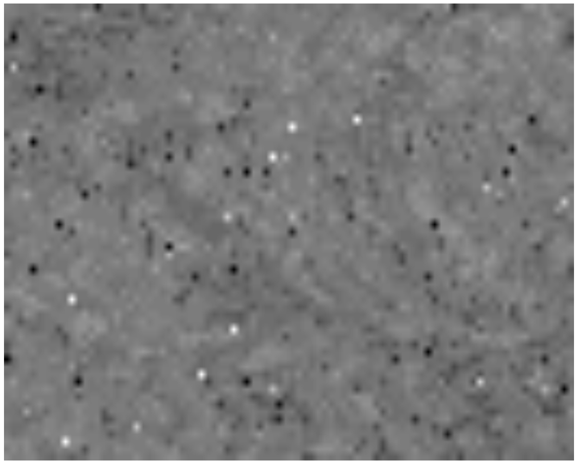
Optical image



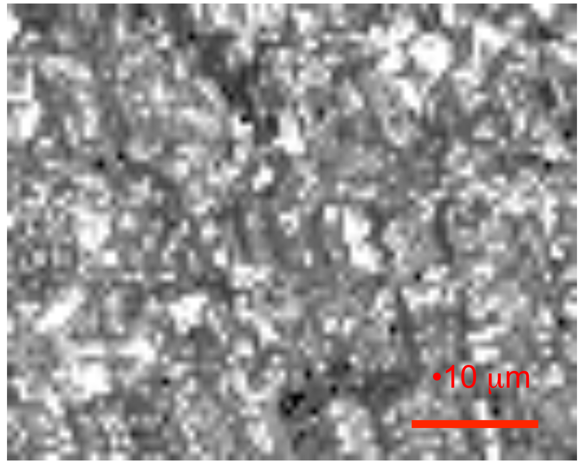
Fresh cathode

R. Kostecki, LBNL

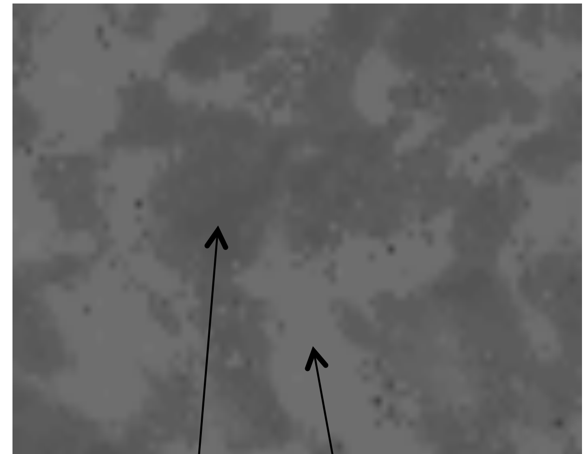
Raman Microscopy: Electrode Structure



Fresh graphitic anode

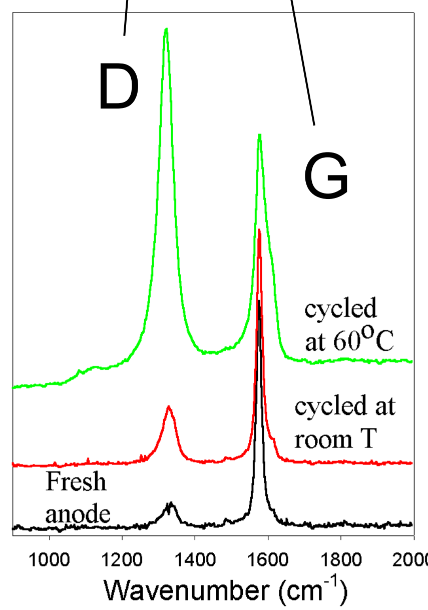


480 cycles, 20˚C, 33% Q_{rev} loss



140 cycles, 60˚C, 65% Q_{rev} loss

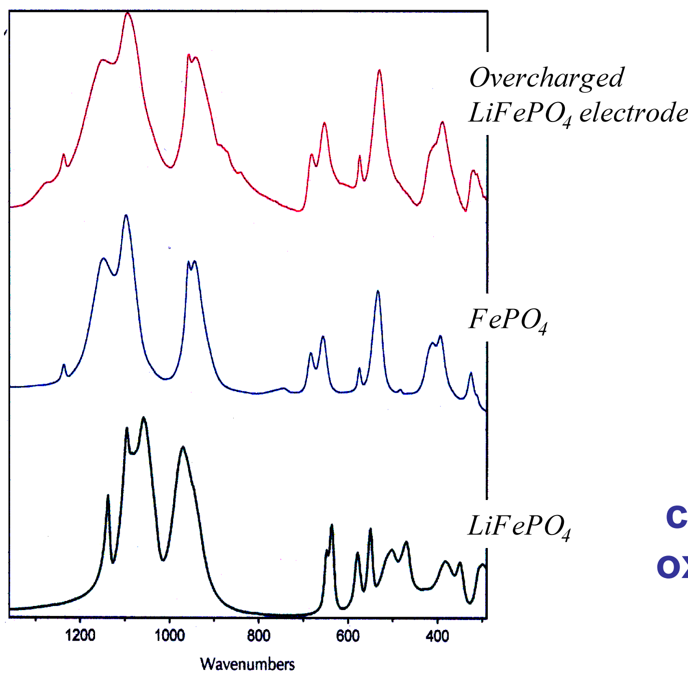
- Specific Raman shifts are characteristic of disordered (D) and graphitic (G) forms of carbon
- Raman images of local D/G ratios identify areas where the original graphitic structure degraded due to cell cycling
- Identified graphite surface degradation as a contributor to cell capacity fade



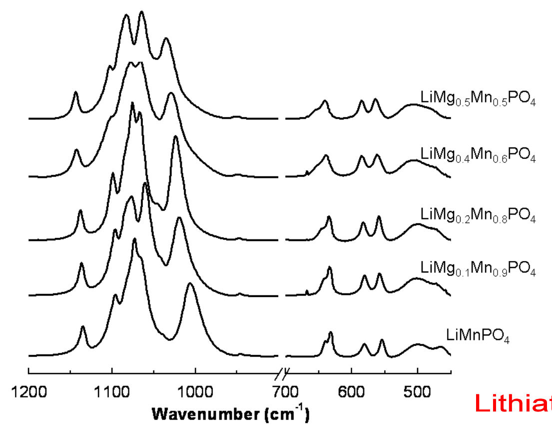
R. Kostecki, LBNL

Infrared Spectroscopy

- Fast, simple, and sensitive to all components regardless of crystallinity
- Qualitative and quantitative analysis
- Sensitive to local coordination and oxidation state

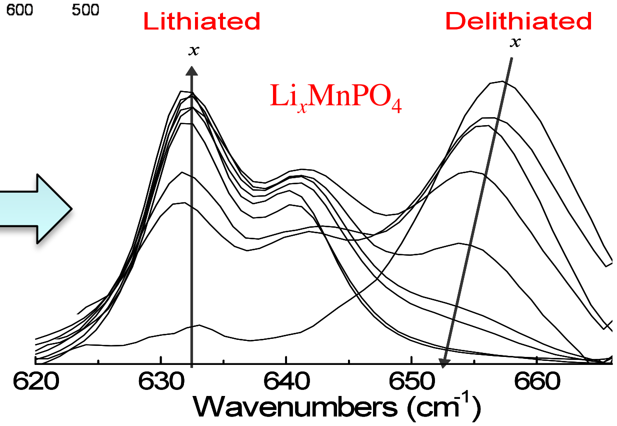


Overcharge products identified



Spectrum changes with substitution

Spectrum changes with oxidation state

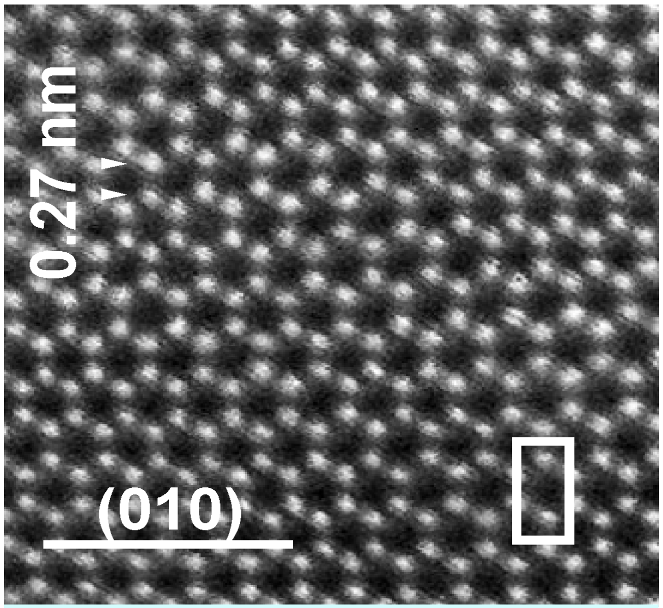


G. Chen and T. J. Richardson, *J. Electrochem. Soc.*, **156**, A756-A762 (2009).

T. Richardson, LBNL

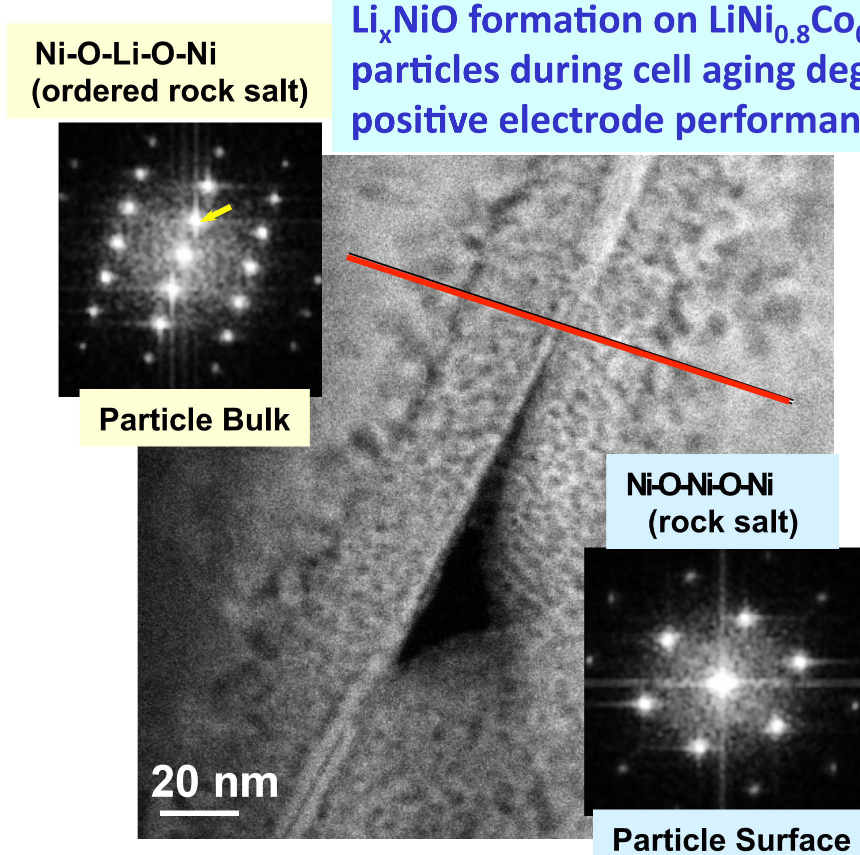
Transmission Electron Microscopy (TEM)

- A thin sample is bombarded with a highly focused electron beam: images and diffraction patterns are formed by interaction of these electrons with the atomic constituents in the sample
- Analysis of TEM images and diffraction patterns yields information on the sample crystal structure and defects that are present



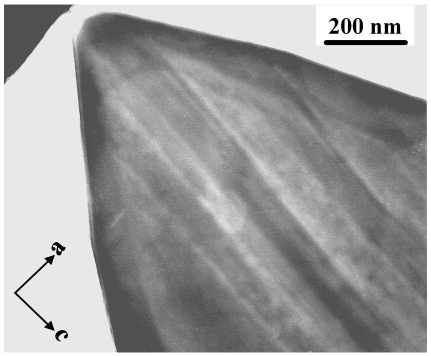
Li_2MnO_3 image showing Li ordering in transition metal (TM) planes. Li columns (dark) are surrounded by Mn columns (bright)

Li_xNiO formation on $LiNi_{0.8}Co_{0.2}O_2$ particles during cell aging degrades positive electrode performance

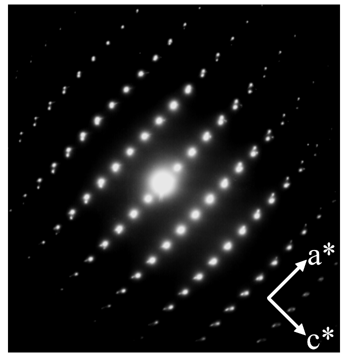


D. Abraham, ANL

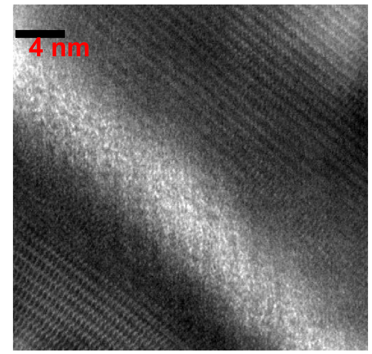
Transmission Electron Microscopy



Detailed structural imaging

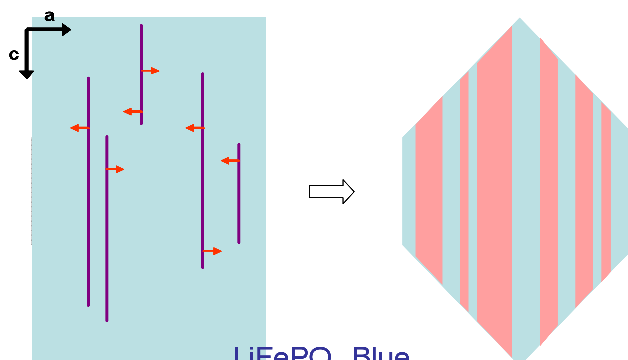


Electron diffraction identifies phases



High-resolution TEM shows phase boundary

G. Chen, X. Song, and T. J. Richardson, *Electrochemical and Solid State Letters*, **9**, A295 (2006).



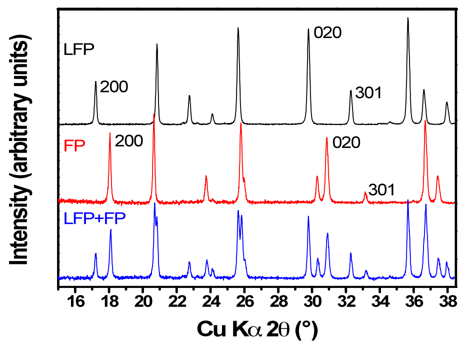
$LiFePO_4$ Blue

$FePO_4$ Red

Identification of charge-discharge mechanisms

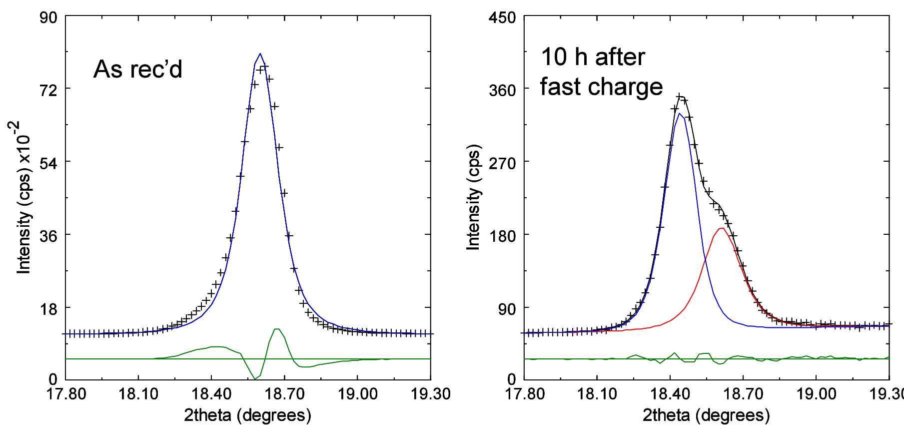
T. Richardson, LBNL

X-Ray Diffraction

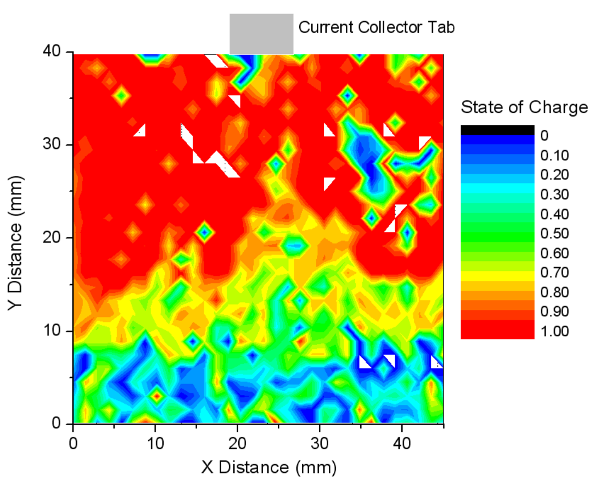


- Qualitative and quantitative analysis of crystalline phases
- Particle size and shape information
- High spatial resolution with small beam sizes

Particle isolation in cathodes following high-temperature storage



G. V. Zhuang, G. Chen, J. Shim, X. Song, P. N. Ross, and T. J. Richardson, *J. Power Sources* **134**, 293-297 (2004).



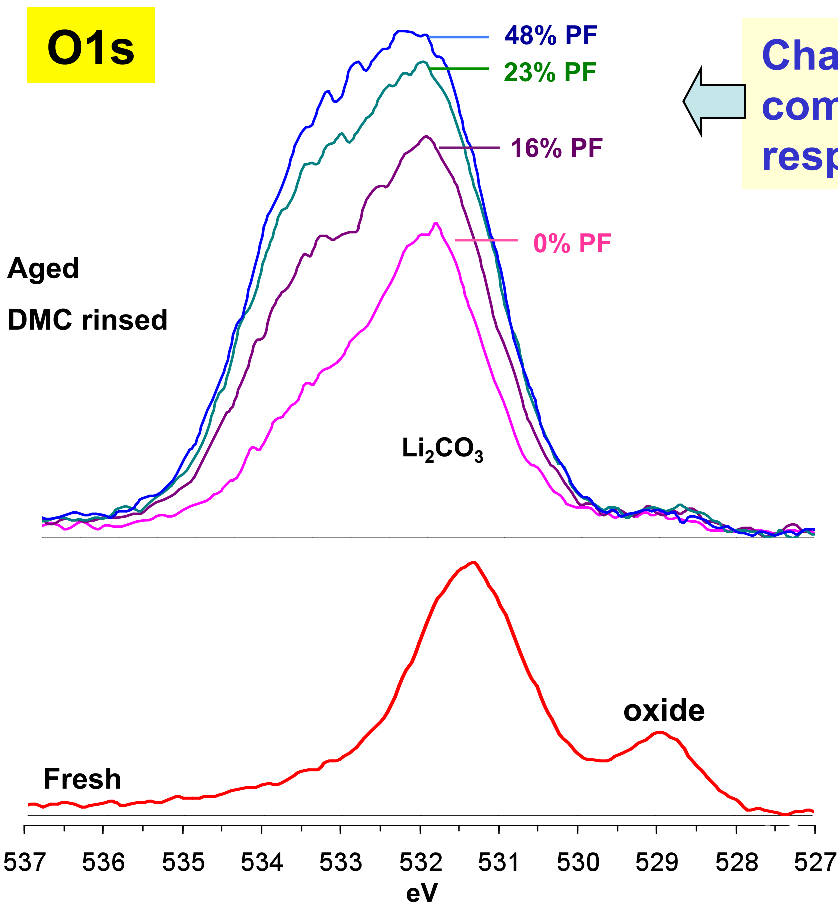
Charge distribution in cycled electrodes

J. Liu, M. Kunz, K. Chen, N. Tamura, and T. J. Richardson, *Journal of Physical Chemistry Letters*, **1** (2010) 2120-2123.

T. Richardson, LBNL

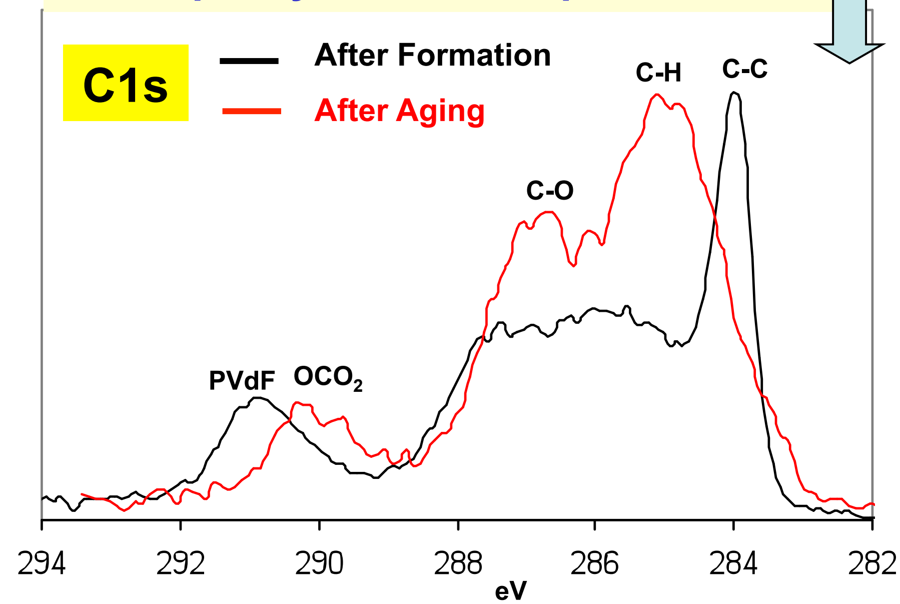
X-ray Photoelectron Spectroscopy (XPS)

- Monoenergetic X-rays eject photoelectrons from a sample, and binding energies of the ejected photoelectrons provide information on sample elemental composition and chemical state
- Well suited for surface analysis of electrode samples



Changes in positive electrode surface film composition and morphology are partially responsible for cell impedance rise

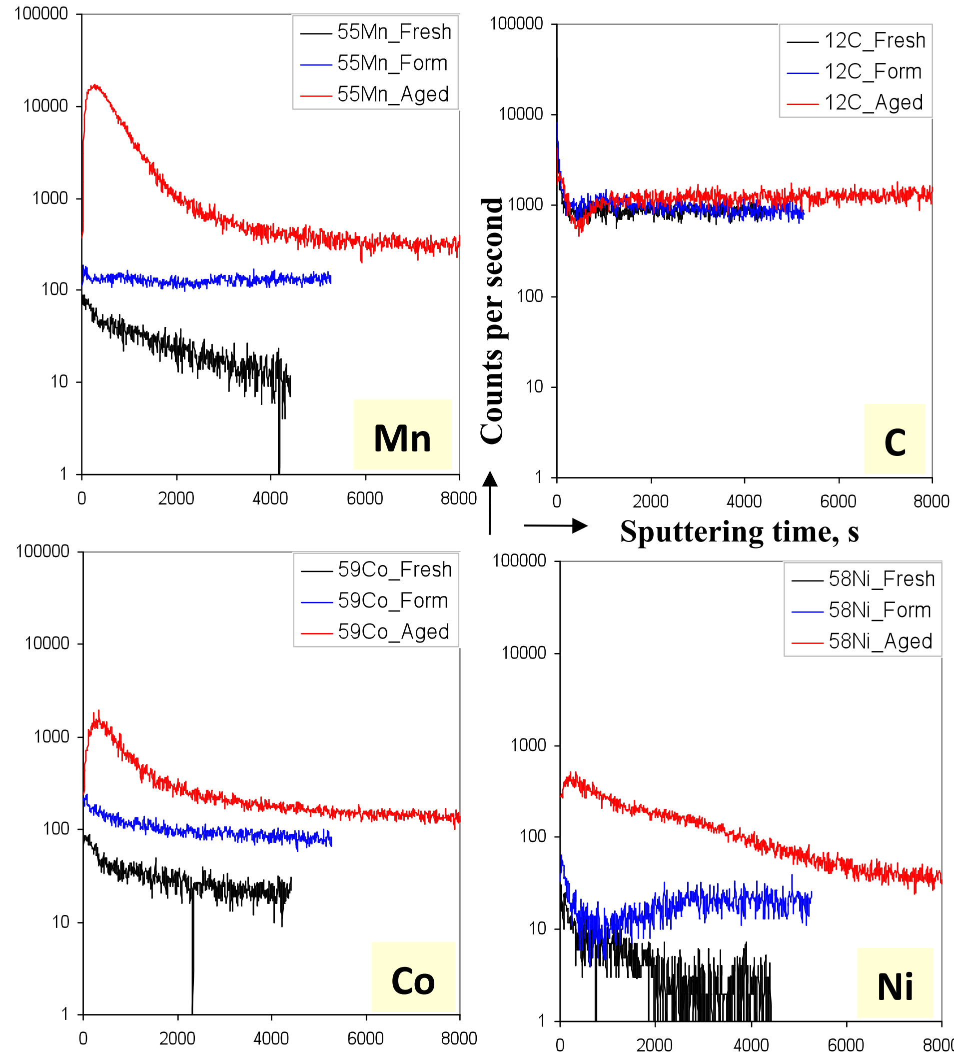
Graphite electrode SEI composition and morphology changes can cause cell capacity fade and impedance rise



D. Abraham, ANL

Secondary Ion mass Spectrometry (SIMS)

- Secondary ions ejected from a sample during bombardment by high-energy primary ions are accelerated into a mass spectrometer, where they are separated according to their mass-to-charge ratio and counted
- Secondary-ion data in static SIMS mode identify composition of the electrode surface (1 - 2 monolayers)
- Dynamic SIMS data reveal electrode composition and trace impurity content as a function of sputtering time (depth)
- Identified transition metal (Mn, Ni, Co) accumulation on graphite electrodes as a catalyst for SEI layer changes that degrade Li-ion cell performance



Dynamic SIMS data on graphite negative electrode

D. Abraham, ANL